

LABORATORY LEACHING BEHAVIOR OF ENVIRONMENTALLY SENSITIVE TRACE ELEMENTS FROM FLY ASH AND BOTTOM ASH SAMPLES

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INTRODUCTION

The distribution of trace elements in coal combustion residues such as fly ash and bottom ash have received considerable attention.^{1,2} Several studies of fly ash have concentrated on relationships of trace elements to fly ash particle size^{3,4,5}. Studies related to etching⁶, mineralogical transformation during combustion⁷ and leaching have also been reported. Dudas⁸ conducted long-term leachability studies. Grisafe et al.⁹ examined leachability of fly ash as a source of Se contamination. Fernandez-Turiel et al.¹⁰ have looked at the mobility of heavy metals from coal fly ash. The objectives of these studies were primarily to understand potential problems associated with the storage or disposal. To meet these objectives, the solvents used in these studies were chosen to emulate conditions in nature.

The leaching study presented in this paper differs from previous leaching studies because the primary objective was to obtain information on modes of occurrence of trace elements in the fly ash and bottom ash and provide data which could be compared to previous studies on the leaching behavior on whole coal samples¹¹. Although preliminary data for 29 elements in the fly ash and bottom ash are available at this time, only results for environmentally sensitive trace elements and other related elements will be discussed in this paper. These elements include those identified in 1990 Clean Air Act Amendments: Co, Cr, Ni, Sb, and radionuclides (Th and U). Fe was also studied because of its importance to coal cleaning and S removal, and Zn because of its relationship to Cd.

EXPERIMENTAL

The samples were collected from an electric utility power plant having boilers burning high sulfur (3.3 weight percent total sulfur) and low sulfur (0.9 weight percent total sulfur) coal. Approximately 10 grams from each of two fly ash samples and two corresponding bottom ash samples were subjected to sequential leaching. In this procedure each sample was automatically shaken for 18 hours, centrifuged, and the leachate filtered. The samples were first leached with 1N ammonium acetate ($\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$). A representative 0.5 gram split of each of the leached samples was reserved for analysis by instrumental neutron activation analysis. This procedure was repeated using 2N hydrochloric acid (HCl), concentrated (48 to 51 %) hydrofluoric acid (HF) and 1.5 N nitric acid (HNO_3) and a representative 0.5 gram split was obtained for INAA from the material leached by each solvent.

All resulting splits and representative samples of the original material were irradiated for 8 hours at a neutron flux of about 2×10^{12} neutrons/cm²sec⁻¹ using instrumental neutron activation analysis (INAA) procedures similar to those of Palmer.¹² The data was calculated using the SPECTRA program.¹³ The mass of each of the splits used to calculate percent material leached and the concentrations for each of the splits determined by INAA were used to calculate the percent of each element leached by each solvent.

RESULTS AND DISCUSSION

The proportion of an element leached by a specific solvent is an indicator of the elements' mode of occurrence. In contrast to coal, which is primarily an organic matrix not leachable to a significant extent by most inorganic solvents, the bottom ash and fly ash are mainly silicates which are leachable to a large degree by inorganic solvents, particularly by HF. In addition, because of the high temperature of combustion ($\sim 1500^\circ\text{C}$) phases present in the coal such as clays, carbonates, and sulfides have also been transformed to silicates and oxides. Table 1 shows the percent of the material leached by each of the solvents used in this study. The total amount of material leached ranged from 78 to 99 percent, with 97 percent or more leached from the fly ashes. Seventy to seventy-nine percent of all samples was leached by HF. Clearly a large percentage of the fly ash and bottom ash are in the silicate phases. Generally less than 5 percent of the fly ash and bottom ash is ammonium acetate soluble (probably water soluble as well). Less than 5 percent of the bottom ash and fly ash is HCl soluble. About 5 to 15 percent of the material was leached by nitric acid. Because sulfides are not likely to be present in the fly ash or the bottom ash (as discussed above) it is not clear which mineral forms were leached by nitric acid. It is possible that species soluble in the nitric acid, unleached by HF, and encased in the silicates during combustion could have been leached only after the destruction of the silicates. It should be noted that the fly ash is generally more soluble in the solvents used in this study than is the bottom ash. This trend may be explained in part by the presence of a larger proportion of unburned carbon in the bottom ash than the fly ash. Preliminary results from CHN analyses and ash determinations showed that up to 18 percent unburned carbon was found in the bottom ash in BA3.

The percentage of some environmentally important elements leached differed from that of the bulk material indicating that their modes of occurrence were clearly different from those of the bulk material. More than 80 percent of the As in the fly ash samples and about 45 percent of the As in one bottom ash sample were leached with HCl. Davidson et al.³ suggest that As, as well as some other elements, may be volatilized during combustion and recondensed on the surface of the particles as they cool in the stack. Turner¹⁴ and EPRI¹⁵ suggest that As may exist as a metal arsenate, such as $\text{Ca}_3(\text{AsO}_4)_2$ or $\text{Ba}_3(\text{AsO}_4)_2$. These suggestions explain why As was leached to a large degree by HCl. The behavior of As in BA3 is different from the other bottom ash sample and from the fly ash samples. Condensation of volatile species such as As is unlikely to occur in bottom ash samples.

Significant quantities of Sb (Figure 2) are leached by HCl in the two fly ash samples; although the amounts are not as large as those for As. Results from a comparison of magnetic and non-magnetic fractions¹⁶ show similarities in behavior between Sb and As. The results of this study however, suggest that Sb and As behave differently.

A few elements, such as U and Th, are leached only to a small degree (as little as 20 percent leached by all solvents). This behavior may be due to their association with minerals such as zircon which are inert and are not significantly altered by either combustion or leaching. Once again these elements are significantly more soluble in fly ash (especially FA1) than in the bottom ash, and U is more soluble than Th. The data for U in fly ash suggests that it may exist in several modes of occurrence because there is roughly equal leaching by HCl and HF in both fly ash samples and equal leaching by HNO_3 in FA1. Figure 3 shows the percentage of these elements leached by each solvent.

Most of the other elements studied show leaching behavior similar to the bulk material. Figure 4 shows the percentage leached for Fe, Ni, Co, and Cr in the bottom ash and the fly ash. In all cases, the majority of these elements are leached by HF, which indicates that they are concentrated in the glassy or crystalline silicates. Most of these elements showed a small amount (<20 percent) of material leached by HCl. Any oxides present are probably locked in the matrix and not exposed until HF destroys the silicates.

Figure 5 shows the percent Zn leached (likely an indicator of Cd behavior). The leaching behavior of Zn is similar to the leaching behavior of the bulk material (Table 1). However, there is a significant fraction of Zn leached by HCl in sample FA3. In addition, about 20 percent Zn was leached by ammonium acetate in sample BA3.

In summary, most, but not all, elements studied behave similarly to the bulk material and are probably associated with the glassy or silicate portions of the fly ash and bottom ash. Because As, U, Th and possibly Sb (in the fly ash) display behavior significantly different than that for the bulk sample, it can be inferred that they are associated with different minerals or chemical forms than the major elements. Other minor differences in the leaching behavior may indicate that small amounts of that element are associated with minor phases in the ash. Some of these minor phases may be material which has not been completely combusted.

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Table 1. Weight percentage of material leached by solvents used in this study.

Solvent	BA1	BA3	FA1	FA3
$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$	1	1	5	3
HCl	2	1	5	3
HF	70	71	78	79
HNO_3	14	5	10	13
Total	86	78	99	97

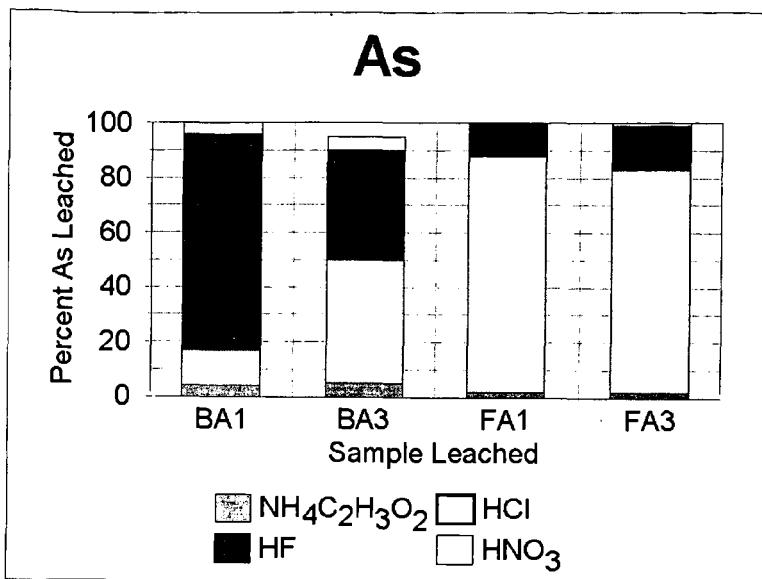


Figure 1. Percent As leached in bottom ash samples (BA1 and BA3) and fly ash samples (FA1 and FA3) by solvents used in this study.

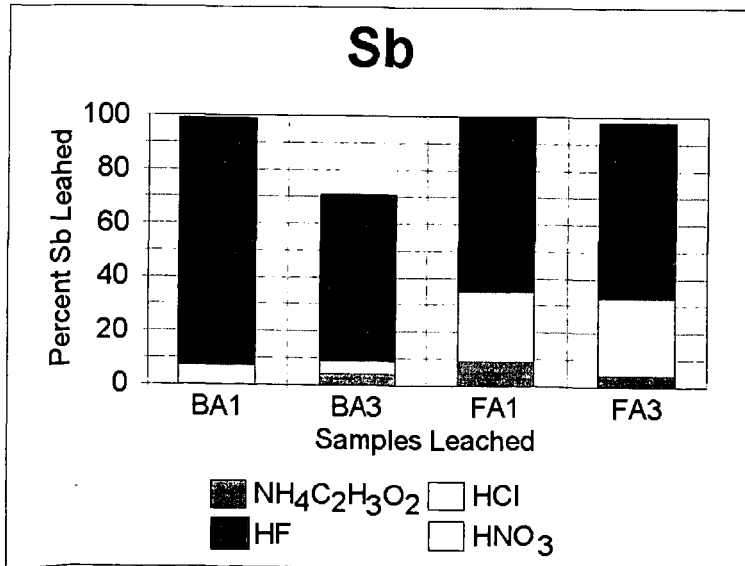


Figure 2. Percent Sb leached in bottom ash samples (BA1 and BA3) and fly ash samples (FA1 and FA3) by solvents used in this study.

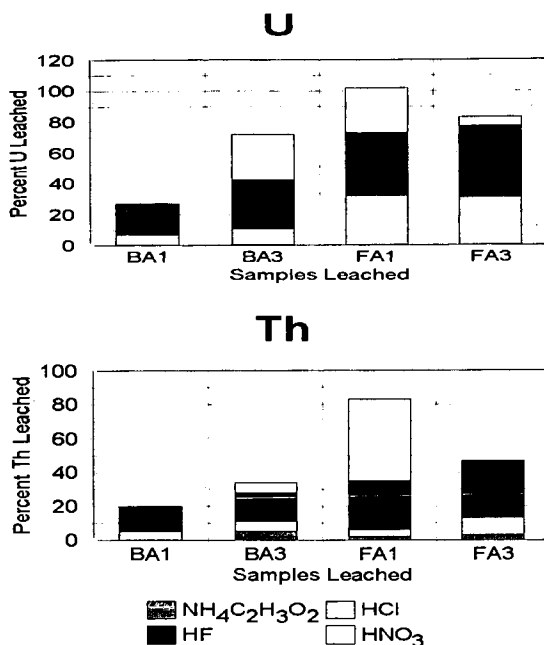


Figure 3. Percent U and Th leached in the bottom ash samples (BA1 and BA3) and the fly ash samples (FA1 and FA3) in this study.

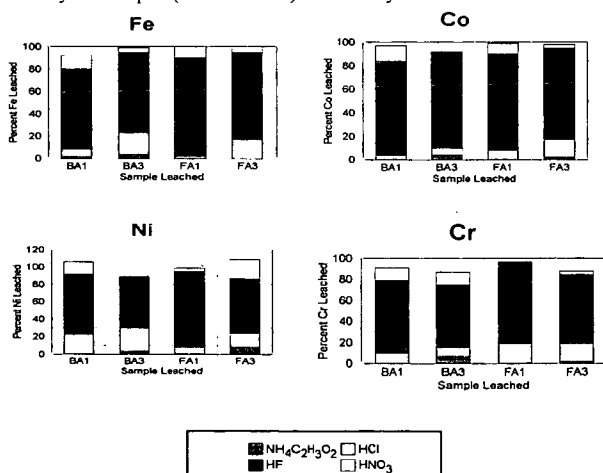


Figure 4 Percent Fe, Co, Ni and Cr leached in the two bottom ash samples and the two fly ash samples by the samples in this study.

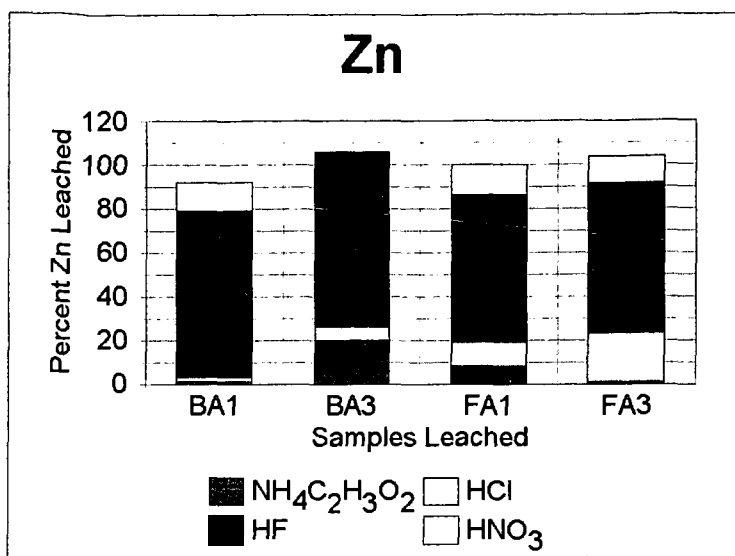


Figure 5. Percent Zn leached in the bottom ash (BA1 and BA3) and fly ash (FA1 and FA3) by solvents used in this study.